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THE INFLUENCE OF FUEL SULFUR ON THE SELECTIVE REDUCTION
OF NO BY NH₃

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I. INTRODUCTION

More intensive regulations of the emissions of nitrogen oxides from stationary combustion sources have prompted the innovation and characterization of new control technologies suitable for applications in utilities. Previously employed technologies were largely based upon the prevention of thermal NO formation, and these are often ineffective in preventing the formations of fuel NO since the two mechanisms depend differently on experimental combustion conditions.

One of the more recent and attractive abatement technologies is the "Thermal DeNO_x" process which has been described by Lyon and Longwell². This process removes NO by selectively reducing it with NH₃ added to the post-combustion gases containing excess oxygen. This process is thus independent of the NO formation mechanism and makes no distinction between thermal and fuel NO.

Our present study is concerned with characterizing the selective reduction process for light distillate oil fuel admixed with variable amounts of pyridene and thiophene in a laboratory scale combustion tunnel under a variety of experimental conditions. This paper will report on those aspects of the study concerned with the investigation of possible synergistic effects between the sulfur and selective reduction chemistry. This is important since some of our remaining fossil fuels have relatively high concentrations of both organically bound sulfur and nitrogen.

Characterization of the selective reduction of NO through reaction with NH₃, added to the post-combustion environment, has involved different types of investigations which provide complementary information. Kinetic studies have been undertaken in a quartz flow reactor by Lyon and co-workers³⁻⁵ to elucidate mechanistic details of the NH₃/NO/O₂ reactions. A recent kinetic modelling study has been undertaken by Miller et al⁶ who were successful in explaining many of the important features of the reactions of NH₃/NO/O₂ in the post-combustion environment. Muzio et al⁷⁻⁸ investigated the selective reduction process for natural gas, a light oil and several types of coal, and have provided some mechanistic information and determined optimum conditions for maximizing the reduction of NO.

Research concerned with the effect of sulfur chemistry on the selective reduction has been inconclusive, and in general relatively little research effort has been directed toward investigating the coupling between nitrogen and sulfur combustion chemistry. Wendt et al⁹ and De Soete¹⁰ have measured fuel nitrogen conversion yields for fuels admixed with sulfur compounds.

II. EXPERIMENTAL

The laboratory scale atmospheric pressure combustion tunnel used in this study consists of three sections: a combustion region, an ammonia injection area, and a reaction and sampling section. Complete, stable, and reproducible burning of a fuel oil/air mixture is accomplished in the first section. Air is supplied by a laboratory compressor through calibrated rotameters to a 5 cm inside diameter low alloy steel tube. The fuel is #1 diesel oil from the Shell Oil Company with a measured hydrogen/carbon ratio of 1.85, 0.04% by weight sulfur, and less than 0.1% by weight nitrogen. Higher concentrations of fuel nitrogen and sulfur are obtained by adding known amounts of pyridine and thiophene, respectively, to the fuel oil delivery tank. The oil is sprayed into the air flow through a commercial high pressure atomizing nozzle (Monarch Type R, 30° radius, 0.05 l/min). Perforated and blocking discs upstream of the nozzle aid in mixing by enhancing the turbulence. A quartz tube at the end of the combustion section allows visual inspection of the flame to confirm that the visible flame front terminates at least 50 cm upstream of the ammonia addition section.

Ammonia (Matheson CP Grade)/nitrogen mixtures are mixed into the combustion products through four symmetrically oriented uncooled quartz injectors. The heavily insulated reaction and sampling section begins immediately downstream of the injectors and extends for ~ 60 cm, where it joins the laboratory exhaust system. There are four different axial locations at which quartz microprobes and/or Chromel/Alumel thermocouples may be inserted to a desired radial location. An aspirated thermocouple is used to correct all reported temperatures for radiation losses. Complete combustion and thorough mixing of the product gases are confirmed by measuring temperature and composition profiles in the reaction region when no ammonia is added. A variety of analytical techniques are used to measure species concentrations, including chemiluminescent analyzers (NO , NO_x), fluorescence detection (SO_2), NDIR (CO , CO_2), GC (many species), and wet chemical methods (NH_3). At the reactant velocities normally used, about 3.8 m/sec, an axial temperature gradient of 1 K/cm was observed. Radial temperature gradients of 20-25 K were measured when the thermocouple was moved from the centerline position to one 80% of the distance to the combustor wall. Concentrations of CO , CO_2 , and NO were found to be independent of probe position, with the CO and CO_2 measurements within experimental error of their calculated equilibrium values. Mixing characteristics of the ammonia injectors were determined by introducing NO through the injector system and then measuring the NO radial and axial profiles downstream. It was found that mixing was essentially complete within 20 cm from the injection site. Concentration profiles of NO and NH_3 measured when reduction occurs indicate that the reaction is essentially finished (>95%) by the final probe station. The data presented in this study are from the centerline position of the final probe position, 59 cm downstream of the ammonia injection site.

III. RESULTS

The reduction of NO by NH_3 addition to the post-combustion gases has been measured as a function of temperature, added NH_3 concentration, and concentration of fuel sulfur. The equivalence ratio in this study was held fixed at a $\phi = 0.89$. Fuel nitrogen was also held constant at 1.02% by weight through the addition of pyridine to the fuel oil. Complete conversion of the fuel nitrogen to NO would result in an NO concentration of ~ 1200 ppm in the exhaust gases. The actual measured concentration before reaction with NH_3 is termed $[\text{NO}]_i$. The temperatures listed, T^* values, are measured at the centerline immediately upstream of the NH_3 injectors. The relative amount of ammonia added is defined by $\beta = [\text{NH}_3]_i/[\text{NO}]_i$.

Prior to determining the effect of fuel sulfur on the NH_3 reduction process, the conversion of fuel nitrogen to NO was measured as a function of fuel sulfur concentration. Table I lists these results for three different fuel sulfur concentrations and various T^* values. With no pyridine added to the fuel, thermal NO concentrations of 40-45 ppm were measured. The thermal concentration was subtracted from the $[\text{NO}]_i$ values when calculating the fuel nitrogen conversion efficiency. The addition of fuel sulfur tends to increase the amount of NO formed from a fixed amount of fuel nitrogen, with only a weak dependence on T^* observed. Measured SO_2 concentrations indicate that within experimental error, quantitative conversion of the fuel sulfur to SO_2 occurs when no NH_3 is present. However, when both sulfur compounds and NH_3 are present, serious errors in the measurements of both species occur because of the formation of sulfur-ammonia species which most likely occurs at the lower temperatures in the probes, sampling lines, or analyzers.

TABLE I				
T^* K	FUEL S ^a %	$[\text{SO}_2]_i^b$ ppm	$[\text{NO}]_i^c$ ppm	% FUEL N CONVERSION TO NO
1170 \pm 5	0.04	—	515 \pm 10	40
1188			510	39
1224			520	40
1252			515	40
1282			515	40
1176 \pm 5	0.33	148 \pm 15	610 \pm 10	48
1200			600	47
1230			615	48
1268			627	49
1293			650	51
1167 \pm 5	0.63		675 \pm 15	53
1194			670	53
1245			705	55

a) added as thiophene; b) measured at terminal probe station with no NH_3 addition; c) added as pyridine (1.02% fuel N)

The temperature dependence of the reduction process is shown in the first three figures. Nitric oxide concentrations are normalized to the initial NO levels measured. Figure 1 illustrates the temperature dependence of the results when no thiophene is added to the fuel. As more ammonia is added (increasing β), greater reduction of NO is obtained. Also, the optimum temperature for reduction increases with increasing β . The effect of increasing the fuel sulfur is shown in Figures 2 and 3. There is a noticeable shift to higher optimum reduction temperatures when the fuel sulfur increases. However, the maximum NO reduction for a fixed β value is not significantly changed. A plot of NO reduction as a function of β at a fixed temperature is shown in Figure 4. At β values less than 1, the fuel sulfur has little effect on the reduction. Above $\beta \approx 1$ the change in the reduction process with increasing fuel sulfur at a constant temperature is more obvious. Preliminary results indicate that this trend continues at even higher fuel sulfur concentrations.

IV. DISCUSSION

The presence of fuel sulfur has two different, though interrelated manifestations: there is an increase in the conversion of fuel nitrogen to NO as the fuel is burned, and the optimum temperature for the NH_3 reduction process shifts to higher values. The observed increase in NO production in the presence of fuel sulfur is in agreement with the results of Wendt et al⁹. Wendt et al added SO_2 or thiophene to fuels doped with NH_3 or pyridine, and showed that the burning characteristics of the fuel were not affected by the addition of an aromatic fuel but rather by the presence of organic sulfur by doping the fuel with benzene in place of thiophene. They reported NO produced to be quite dependent on the method of mixing the fuel and air. It is very difficult, however, to quantitatively characterize "mixing" in a turbulent diffusion flame. In our study the flow conditions were held constant and there were no visible differences in the flames when thiophene was present. Since we have made no attempt to observe reaction intermediates during the combustion of fuel nitrogen, we can only speculate as to the cause of the increased NO formation.

The dependence of the selective reduction of NO by NH_3 on temperature and β has been reported previously.^{7,8} When no thiophene is added to the pyridine/oil mixture (0.04% fuel sulfur) the results in terms of NO reduction levels and temperatures for achieving optimum reduction are essentially identical to those obtained when NO is injected in the air supply (replacing the pyridine in the fuel) to produce a downstream NO concentration of ~ 500 ppm.¹¹ Sulfur compounds in the post-combustion gases could affect the reduction process by reacting with the ammonia or an ammonia derived species, effectively lowering the concentration of the reducing agent

(lower β). This would result in less NO reduction and in a decrease in the temperature for achieving the optimum NO reduction. Neither of these is observed. Lower concentration of SO₂ and NH₃ are measured when both species are present, but this is most likely attributable to reactions in the sampling system. The observed shift in the optimum temperature suggests a change in the reaction mechanism, or the presence of a competing reaction pathway when sulfur compounds are present. Sulfur dioxide has been identified as the major product of sulfur compounds in lean combustion environments; however other sulfur compounds present in significantly smaller concentrations could also be important. Additional research is warranted to further elucidate the role of various sulfur compounds in nitrogen combustion chemistry.

ACKNOWLEDGEMENT

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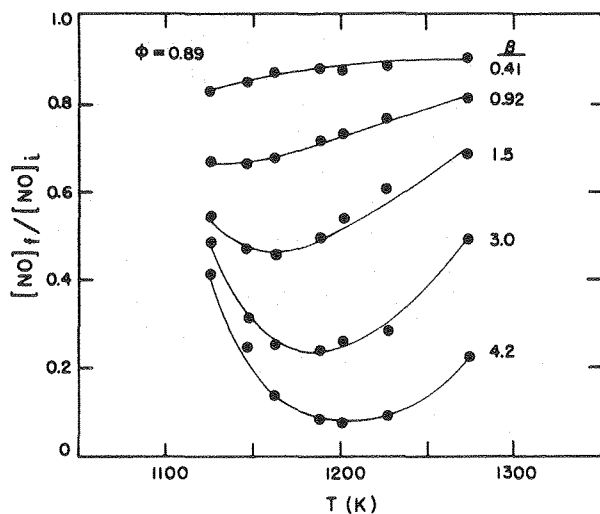


Figure 1. NO reduction as a function of temperature with no thiophene added to fuel (0.04% fuel S).

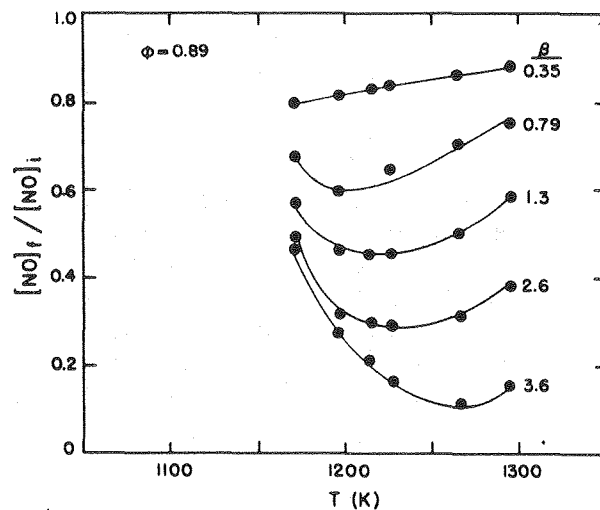


Figure 2. NO reduction with thiophene addition (0.33% fuel S).

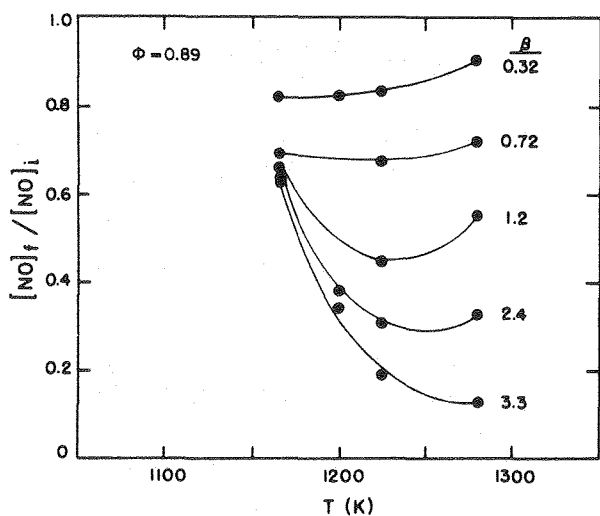


Figure 3. NO reduction with thiophene addition (0.63% fuel S).

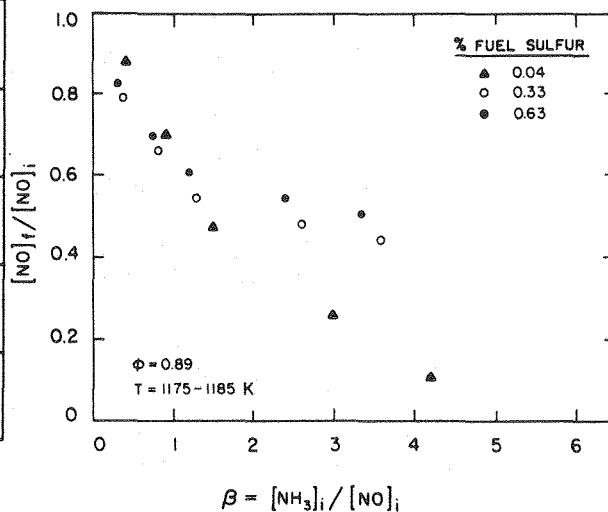


Figure 4. NO reduction at a constant temperature as a function of added NH_3 .